

Ingalls R. Electric-field gradient tensor in ferrous compounds.
Phys. Rev. A 133:787-95, 1964.
[Carnegie Institute of Technology, Pittsburgh, PA]

This paper presents a theory of the nuclear electric quadrupole splittings in divalent iron compounds as measured by the Mössbauer effect. The great variety in temperature dependent electric field gradient tensors in many such compounds is satisfactorily explained in terms of the combined effects of the crystalline field, spin-orbit interaction, covalency, and Sternheimer polarization. [The SC1® indicates that this paper has been cited in over 485 publications since 1964.]

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"In 1960, while a graduate student under the direction of Sergio DeBenedetti at Carnegie Institute of Technology, I found myself measuring the Mössbauer effect in some iron compounds. This new research tool was a hot topic. To the amazement of those in the laboratory, including George Lang and Romeo Segnan, divalent compounds of Fe⁵⁷ appeared to not only exhibit the usual resonance line near a (Doppler) velocity of zero, but also a second line far to one side. This was the first evidence of the large nuclear quadrupole splitting in such compounds¹ and was also observed at about the same time by G.K. Wertheim.² Shortly afterward came our paper³ interpreting the large splittings in terms of crystalline field effects and also including a quantitative explanation of the nuclear volume effect. (The latter has been occasionally called the isomer shift.)

"At that time two main questions remained regarding a more quantitative interpretation of the

quadrupole splittings in ferrous compounds. These were the role of Sternheimer antishielding and a more refined treatment of the effect of the crystal field plus spin-orbit interaction, which particularly affected the temperature dependence. My thesis research covered the first of these topics. Afterward, I continued to explore the role of the crystalline field and was thunderstruck by the realization that it was also directly responsible for the lattice contribution to the electric field gradient at the nucleus. This study found me forever waiting in line to receive some computer output, since the work heavily relied on the diagonalization of large matrices. I can recall Lang and DeBenedetti shaking their heads over the large computer bills accruing to the research contract.

"The results of this work were significant in that a detailed interpretation of the quadrupole splittings in ferrous compounds enabled one to probe the electronic structure and local surroundings of the Fe²⁺ ion. More generally, chemists, metallurgists, biophysicists, etc., use both the quadrupole splittings and isomer shifts to identify the valence and spin state of iron atoms in their samples, as well as the more detailed structural information. Such work was a model for understanding the quadrupole interaction in low-spin Fe(III) compounds and also for the analysis of experiments with other Mössbauer isotopes.

"I tend to feel the qualitative interpretation of the ferrous quadrupole interaction, that is, the reason behind the marked temperature dependence and great range in low temperature splittings, to be of more significance than the actual quantitative results. A few researchers may disagree, however, pointing out the great interest, for example, in a numerical value for the electric quadrupole moment of the first excited state of Fe⁵⁷. As a matter of fact, the 'best' value for this quantity took perhaps another ten years to stabilize, amidst amazingly serious controversy as to the proper wave functions, covalency treatment, lattice field gradient, antishielding factors, spin-orbit constant, etc. I regard two subsequent papers^{4,5} as characteristic extensions of this work. The subject is treated in reviews on the Mössbauer effect."^{6,7}

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